

AN INTRODUCTION TO MCSCF

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ORBITAL APPROXIMATION

$$\psi_{\text{hp}} = \psi_1(1) \psi_2(2) \dots \psi_N(N)$$

- Hartree product (hp) expressed as a product of spinorbitals $\psi_i = \phi_i \alpha_i$
- ϕ_i = space orbital, α_i = spin function (\uparrow , \downarrow)
- Pauli Principle requires antisymmetry:

$$\psi = \hat{A} \psi_{\text{hp}} = \frac{1}{\sqrt{N!}} |\psi_1(1) \psi_2(2) \dots \psi_N(N)|$$

ORBITAL APPROXIMATION

- For more complex species (one or more open shells) antisymmetric wavefunction is generally expressed as a linear combination of Slater determinants
- Optimization of the orbitals (minimization of the energy with respect to all orbitals), based on the Variational Principle) leads to:

HARTREE-FOCK METHOD

- Optimization of orbitals leads to
 - $F_i = \epsilon_i \phi_i$
 - $F =$ Fock operator $= h_i + \epsilon_i(2J_i - K_i)$ for closed shells
 - $\phi_i =$ optimized orbital
 - $\epsilon_i =$ orbital energy

HARTREE-FOCK METHOD

- Closed Shells: Restricted Hartree-Fock (RHF)

$$= \left| \begin{array}{ccccc} \bar{1} & \bar{1} & \bar{2} & \bar{2} & \cdots & \bar{N} & \bar{N} \end{array} \right|$$

- Consider H_2 : $= \left| \begin{array}{cc} \bar{1} & \bar{1} \end{array} \right|$

- The 2-electron case can be written more simply

$$= \frac{1}{\sqrt{2}} [\phi_1(1)\phi_1(2) - \phi_1(2)\phi_1(1)] \frac{1}{\sqrt{2}} =$$

- $= (\text{space function}) (\text{spin function})$

- Simplest MO for H_2 is minimal basis set:
- $\psi_1 = [2(1+S)]^{-1/2} (1s_A + 1s_B)$
 - $1s_A, 1s_B$ = AOs on H_A, H_B , respectively
- Expectation value of energy $\langle E \rangle$ is
 - $\langle E \rangle = \langle \psi_1 | \hat{H} | \psi_1 \rangle = \langle \psi_1 | \hat{H} | \psi_1 \rangle / \langle \psi_1 | \psi_1 \rangle$
 - Since H is spin-free, so
 - Main focus is on space part:
 - $\psi_1 = \frac{1}{\sqrt{2(1+S)}} (1s_A(1) + 1s_B(1)) (1s_A(2) + 1s_B(2))$
 - $\langle E \rangle = [2(1+S)]^{-1} [1s_A(1) + 1s_B(1)] [1s_A(2) + 1s_B(2)]$

- $$= [2(1+S)]^{-1} [1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) + 1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)]$$
- 1st 2 terms = ionic, 2nd 2 terms = covalent
 - $$= [2(1+S)]^{-1} [\psi_{\text{ion}} + \psi_{\text{cov}}]$$
 - So, HF wavefunction is equal mix of covalent & ionic contributions
 - Apparently OK ~ equilibrium geometry
 - Consider behavior as $R \rightarrow \infty$: $S \rightarrow 0$
 - $$\rightarrow 1/2 [\psi_{\text{ion}} + \psi_{\text{cov}}]$$
 - $$\langle E \rangle \rightarrow 1/4 \langle \psi_{\text{ion}} + \psi_{\text{cov}} | H | \psi_{\text{ion}} + \psi_{\text{cov}} \rangle$$

- The Hamiltonian is

$$H = H_1^{(0)} + H_2^{(0)} + 1 / r_{12}$$

$$H_1^{(0)} = -(1/2) \frac{\partial^2}{\partial r_1^2} - Z_A / r_{A1} - Z_B / r_{B1}$$

- Plugging in & recognizing that as $R \rightarrow \infty$, many terms $\rightarrow 0$:

$$- \langle E \rangle_{R \rightarrow \infty} \rightarrow 1/2[(E_{H^+} + E_{H^-}) + 2E_H]$$

- So, the HF wavefunction gives the wrong limit as H_2 dissociates, because ionic & covalent terms have equal weights.
- Must be OK $\sim R_e$, since HF often gives good geometries
- HF/MBS $D_e \sim 3.64$ ev. Cf., $D_e(\text{expt}) \sim 4.75$ ev

VALENCE BOND METHOD

- Alternative to MO, originally called Heitler-London theory
- *Presumes a priori* that bonds are covalent:
 - $\psi_1 = 1s_A(1)1s_B(2); \quad \psi_2 = 1s_A(2)1s_B(1)$
 - $\psi_{VB} = [2(1+S_{12})]^{-1/2} [\psi_1 + \psi_2]; \quad S_{12} = \langle \psi_1 | \psi_2 \rangle = S_{AB}^2$
- Apply linear variation theory in usual way:
 - Dissociation to correct limit $H + H$
 - $D_e \sim 3.78 \text{ eV}$; cf., $D_e(\text{expt}) \sim 4.75 \text{ eV}$.

- So, the MO wavefunction gives the wrong limit as H_2 dissociates, whereas VB gives correct limit.
- Both MO and VB give poor D_e
- MO incorporates too much ionic character
- VB completely ignores ionic character
- Both are inflexible
- How can these methods be improved?

IMPROVING VB AND MO

- Could improve VB by adding ionic terms using variational approach:
 - $VB_{imp} = VB + c_{ion} = c_{cov} + c_{ion}$
 - where c = variational parameter.
 - Expect $c_{ion} \sim 1$ $\sim R=R_e$ & $c_{cov} \rightarrow 0$ as $R \rightarrow \infty$
- Since MO method over-emphasizes ionic character, want to do something similar, but in reverse

IMPROVING VB AND MO

- Improve MO by allowing electrons to stay away from each other: decrease importance of ionic terms. Recall (ignoring normalization)
 - $\psi_{\text{MO}} = \psi_1(1) \psi_1(2): \psi_1 = 1s_A + 1s_B$
- Antibonding orbital
 - $\psi_{\text{MO}}^* = \psi_2(1) \psi_2(2): \psi_2 = 1s_A - 1s_B$
 - Keeps electrons away from each other.

- So, we write (ignoring normalization)

$$- \quad \text{MO}_{\text{imp}} = \text{MO} + \text{MO}^* = \phi_1(1) \phi_1(2) + \phi_2(1) \phi_2(2)$$

– where λ = variational parameter

– $\lambda \rightarrow 0$ at $R = R_e$

– $\lambda \rightarrow 1$ as $R \rightarrow \infty$

- Can easily show that

$$- \quad \text{MO}_{\text{imp}} = \text{VB}_{\text{imp}}; \quad \lambda = (1 + \epsilon)/(1 - \epsilon)$$

- MO_{imp} is simplest MCSCF wavefunction

– Gives smooth dissociation to $\text{H} + \text{H}$

RHF VS. UHF

- Recall that
 - $\psi_1 = [2(1S)]^{-1/2} (1s_A + 1s_B)$: bonding MO
 - $\psi_2 = [2(1S)]^{-1/2} (1s_A - 1s_B)$: anti-bonding MO

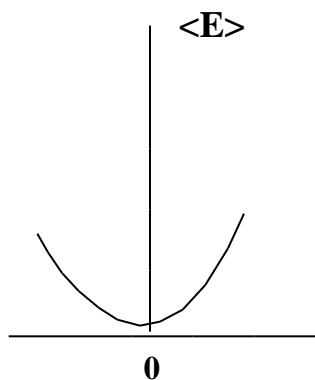
- Ground state wavefunction is

$$= |\psi_1 \bar{\psi}_1|$$

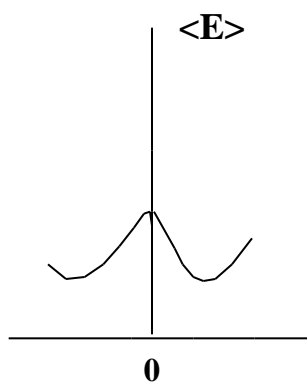
- Ground state space function $\psi = \psi_1(1) \psi_1(2)$
- RHF since ψ , electrons *restricted* to same MO

- Can introduce flexibility into the wavefunction by relaxing RHF restriction.
 - Define two new orbitals ϕ_1, ϕ_2 , so that
 - $\Psi_{\text{UHF}} = \phi_1(1)\phi_2(2)$: Unrestricted HF/UHF, different orbitals for different spins: DODS
- Can expand these 2 UHF orbitals in terms of 2 known linearly independent functions. Take these to be ϕ_1, ϕ_2 :
 - $\phi_1 = \phi_1 \cos \theta + \phi_2 \sin \theta \quad \theta = 0 \text{ to } 45^\circ$
 - $\phi_2 = \phi_1 \cos \theta - \phi_2 \sin \theta \quad \theta = 0^\circ$: RHF solution

- Can expand ψ_1, χ_1 in terms of $1s_A, 1s_B$
- Then derive $\langle E \rangle, d\langle E \rangle/d, d^2\langle E \rangle/d^2$
 - Details in Szabo & Ostlund; 2 possibilities:



RHF solution: stable



RHF unstable: UHF

- Corresponds to Pople RHF/UHF stability test

- As H-H bond in H_2 is stretched,
 - Optimal value of θ must become nonzero, since
 - We know RHF solution is incorrect at asymptote
 - As $R \rightarrow \infty$, $\theta \rightarrow 45^\circ$
 - Can express UHF wavefunction as

$$\psi_{UHF} = \cos^2 \theta \left(\frac{1}{\sqrt{2}} \left(\phi_1 \bar{\phi}_1 + \phi_2 \bar{\phi}_2 \right) \right) - \sin^2 \theta \left(\frac{1}{\sqrt{2}} \left(\phi_1 \bar{\phi}_2 + \phi_2 \bar{\phi}_1 \right) \right)$$

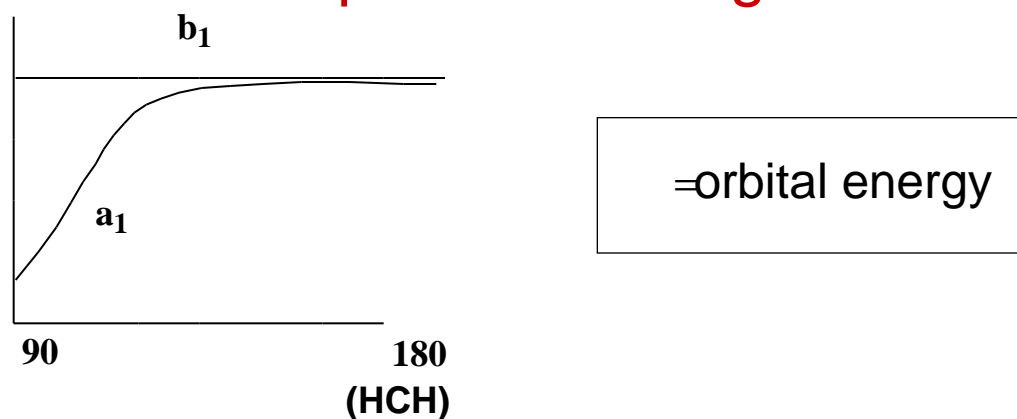
- Note that 1st 2 terms are just MCSCF wavefunction
- 3rd term corresponds to spin contamination

$$\psi_{UHF} = \cos^2 \theta \left| \begin{array}{c} \bar{1} \\ 1 \end{array} \right| - \sin^2 \theta \left| \begin{array}{c} \bar{2} \\ 2 \end{array} \right| - \sin \theta \cos \theta \left\{ \left| \begin{array}{c} \bar{1} \\ 2 \end{array} \right| - \left| \begin{array}{c} \bar{2} \\ 1 \end{array} \right| \right\}$$

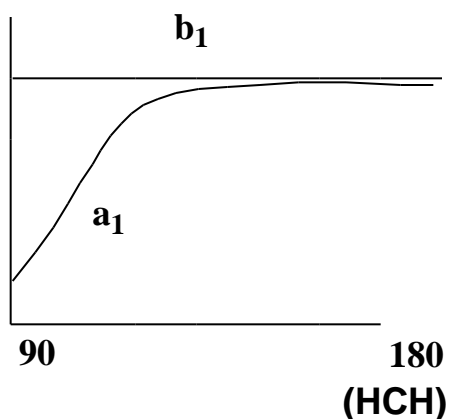
- At $\theta = 0^\circ$, $\psi_{UHF} = \psi_{RHF} = \left| \begin{array}{c} \bar{1} \\ 1 \end{array} \right|$
- At $\theta = 45^\circ$, $\psi_{UHF} = 1/2 \left| \begin{array}{c} \bar{1} \\ 1 \end{array} \right| - 1/2 \left| \begin{array}{c} \bar{2} \\ 2 \end{array} \right| - 1/2 \left\{ \left| \begin{array}{c} \bar{1} \\ 2 \end{array} \right| - \left| \begin{array}{c} \bar{2} \\ 1 \end{array} \right| \right\}$
- So, UHF wavefunction correctly dissociates to H + H, but wavefunction is 50-50 mixture of singlet and triplet
- UHF therefore gives non-integer natural orbital occupation numbers.

SINGLET CH_2

- Consider simple Walsh diagram



- In H_2O , a_1 , b_1 both doubly occ lone pairs: HF OK
- b_1 = pure p HOMO, a_1 s character $\rightarrow 0$ as $\rightarrow 180^\circ$
- At $=180^\circ$, (a_1, b_1) become degenerate orbital



- In CH_2 , $a_1=\text{HOMO}$, $b_1=\text{LUMO}$
- At $=90^\circ$, $N(a_1)\sim 2$, $N(b_1)\sim 0$: HF OK
- At $=180^\circ$, (a_1, b_1) = degenerate orbital, so

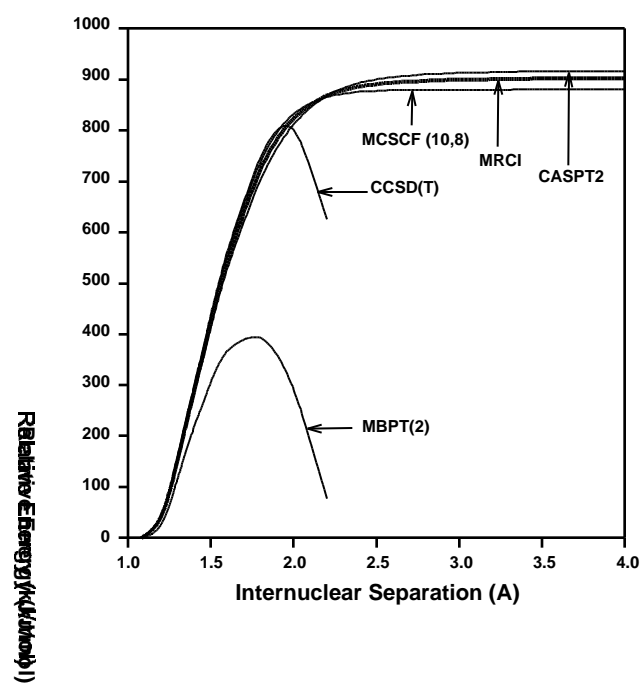
$$= (2)^{1/2} \{ |a_1 \bar{a}_1| - |b_1 \bar{b}_1| \}$$
- There are 2 equally weighted configurations

- Most general form of $^1\text{CH}_2$ wavefunction is

$$= C_1 | a_1 \bar{a}_1 | + C_2 | b_1 \bar{b}_1 |$$

- This is a FORS or CASSCF wavefunction:
 - 2 active electrons in 2 active orbitals: (2,2)
 - At $\sim 90^\circ$: $C_1 \sim 1$, $C_2 \sim 0$: NOON $\sim 2,0$
 - At $= 180^\circ$: $C_1 = C_2 = 2^{-1/2}$: NOON $\sim 1,1$

- Now consider N_2 dissociation:
 - Breaking 3 bonds: $\rightarrow + 2$
 - Minimum correct FORS/CASSCF=(6,6)
 - Used as benchmark for new methods designed for bond-breaking
 - Head-Gordon
 - Piecuch



MCSCF

- Usually scales $\sim N^{5-6}$, but can be worse
- Necessary for
 - Diradicals
 - Unsaturated transition metals
 - Excited states
 - Often transition states
- CASSCF accounts for near-degeneracies
- Still need to correct for rest of electron correlation: “dynamic correlation”

MULTI-REFERENCE METHODS

- **Multi-reference CI: MRCI**
 - CI from set of MCSCF configurations
 - Most commonly stops at singles and doubles
 - MR(SD)CI
 - Very demanding
 - ~ impossible to go past 14 electrons in 14 orbitals
- **Multi-reference perturbation theory**
 - More efficient than MRCI
 - Not usually as accurate as MRCI

